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# Optical properties of Be and Mg from APW band calculations

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The non-relativistic augmented plane wave band calculations of Chatterjee & Sinha for Be and Mg have been used to calculate the imaginary part, $\epsilon_2(\omega)$, of the dielectric function for these metals via the joint density of states (JDOS) and the double energy density of states (DEDOS) for their optical transitions at zero temperature. From these calculations it has been possible to identify the bands and the portions of the Brillouin zone (BZ) mainly responsible for the peaks in the JDOS and the DEDOS curves, together with the frequencies where such peaks occur. We observe that Be, whose energy bands deviate markedly from those of free electrons, shows only one major peak in its JDOS curve, while Mg, which is free electron-like has three well-defined peaks. The results further indicate that such peaks can arise from transitions away from the symmetry points and lines in the BZ.

## 1. INTRODUCTION

The study of the electronic energy bands of divalent hexagonal close packed (hcp) metals has been the subject of varied investigations (Loucks & Cutler 1964, Falicov 1962, Harrison 1962, Terrell 1964, 1966, Stark & Falicov 1967, Dommock 1971, Chatterjee & Sinha 1975, Sinha & Chatterjee 1977) because of the extra richness of their electronic properties. Knowledge of the electron energy bands of such crystals is of primary importance not only for studying their electronic behaviour but also for studying the effects of electronic excitations on other excitations of the crystal. One of the important quantities which can be predicted from these band structure data is the imaginary part of the optical dielectric function for interband transitions of bound electrons, viz., $\epsilon_2^b(\omega)$. Recently, Weaver, Lynch & Olson (1973, 1974) have obtained the value of this dielectric function from absorptivity experiments on the bcc transition metals, Nb and Mo over a wide range of frequencies. In view of these, our predictions will not only serve as a tool for testing the reliability and the usefulness of the particular method used for calculating the energy bands theoretically, via the comparison of the theoretical and experimental dielectric functions (when such experiments are performed on hcp metals) but also serve to identify the location in $\boldsymbol{k}$-space of the important optical excitations of these metals.

In this paper we have used the Augmented Plane Wave (APW) calculations of the energy bands of Be and Mg by Chatterjee & Sinha (1975) to calculate the variation of $c_2{}^b(\omega)$ with the frequency of the exciting radiation. The calculation allows us to identify the bands chiefly responsible for, and the location in $\boldsymbol{k}$-space where, the important peaks occur, together with the frequencies, they correspond to.

## 2. Outline of the Method

The photon energy distribution function, $D(\omega)$, for the total number of allowed transitions between the occupied and the unoccupied parts of various bands for photon energies between $\omega$ and $\omega+\Delta\omega$ is given by

$$D(\omega) = \sum_{\substack{E_l,\,E_u \\ l\pm u \\ E_u-E_l=\omega}} \int f\{E_l(\boldsymbol{k})\}[1-f\{E_u(\boldsymbol{k})\}]d^3k \;\; |<u|\boldsymbol{p}|l>|^2 \times \delta\{E-E_u(\boldsymbol{k})\}\delta\{E-\omega-E_l(\boldsymbol{k})\} \quad \ldots (1)$$

where $f$ is the Fermi Function, $<u|\boldsymbol{p}|l>$ is the momentum matrix element, and $E_u(\boldsymbol{k})$ and $E_l(\boldsymbol{k})$ are the energies of an electron with wave vector $\boldsymbol{k}$ in the upper band, $u$, and the lower band, $l$, respectively. The function $D(\omega)$ is proportional to $\omega^2 c_2{}^b(\omega)$, where $c_2{}^b(\omega)$ is the imaginary interband part of the dielectric function for bound electrons.

Now the matrix elements in equation (1) are time consuming to include in a complete BZ integration. The approximation of constant matrix elements; which will be used throughout this paper, is believed to affect only the strength of the peaks (Pickett & Allen 1975, Koelling *et al.* 1974). However, this approximation may shift the position of the peaks slightly depending on the crudeness of the approximation but in no case will there be a suppression of the peaks as the matrix elements are believed to be nonoscillatory functions of the energy. In this approximation, therefore, $D(\omega)$ becomes a function of the joint density of states (JDOS) for optical transitions, defined by

$$\sum_{\substack{E_l,\,E_u \\ l\pm u \\ E_u-E_l=\omega}} \int f\{E_l(\boldsymbol{k})\}[1-f\{E_u(\boldsymbol{k})\}]d^3k\delta\{E-E_u(\boldsymbol{k})\}\delta\{E-\omega-E_l(\boldsymbol{k})\} \quad \ldots (2)$$

while the double energy density of states (DEDOS), which permits one to study the number of momentum—conserving transitions as a function of the initial energy, $E' = E-\omega$, and the final energy, $E$, is given by

$$I(E, E') = \int f\{E_l(\boldsymbol{k})\}[1-f\{E_u(\boldsymbol{k})\}]d^3k\delta\{E-E_u(\boldsymbol{k})\}\delta\{E'-E_l(\boldsymbol{k})\}. \quad \ldots (3)$$

As the theoretical APW calculations are valid at 0°K, the quantity $f\{E_l(\boldsymbol{k})\}\times[1-f\{E_u(\boldsymbol{k})\}]$ in equations (1), (2) and (3) will be taken to be unity throughout this paper.

Now to find the density of states (DOS), the JDOS and the DEDOS, the irreducible wedge of the hexagonal BZ (figure 1) was divided into a large number

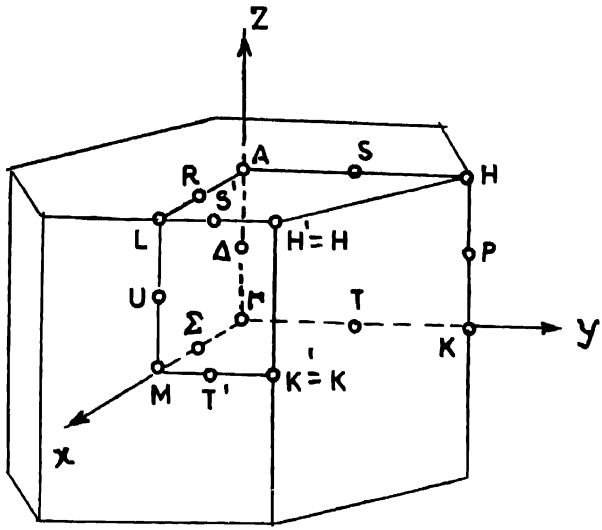


Fig 1. Brillouin zone for the hexagonal Bravais lattice, with symmetry notations of Herring

of microhexagons. The energy in each microzone was found out partly from the APW energy band calculation (1975) and partly, where this was not possible, from an interpolation scheme. Gilat-Raubenheimer (1966) and Pickett *et al* (1975) have used an alternative method to calculate the DOS and the JDOS respectively, where the energy values at limited $\boldsymbol{k}$-points inside the BZ were sufficient. These calculations are rather heavy and require the energy gradient at each $\boldsymbol{k}$-point However, as Janak (1971) has pointed out, if a large number of energy values are available inside the BZ, it is sufficiently accurate to calculate the DOS, the JDOS and the DEDOS by means of the ordinary stabilised histogram method which, according to him may be thought to be a zeroth order fit to energy surfaces as compared to the first order fit of the Gilat-Raubenheimer method

## 3. Results

To calculate the DOS, the JDOS and the DEDOS we have made use of the APW energy band diagrams of Chatterjee & Sinha (1975) along the symmetry points and axes of the hexagonal BZ. However, since these quantities involve

the entire volume of the BZ, the data of those figures alone were not sufficient for obtaining a reliable DOS, JDOS or DEDOS curve. For this purpose, the irreducible 1/24th part of this BZ was divided into 216 microzones as was done by Loucks & Cutler (1964) The energy values at the centres of these microzones were obtained by graphical interpolation from the data of the above mentioned figures. This procedure, although very crude, nevertheless gives energies at equally spaced points inside the BZ which is essential for the DOS, the JDOS and the DEDOS

The JDOS for the optical transitions of Be and Mg are depicted in figures (2) and (3) respectively. The stable JDOS histograms correspond to $\Delta E$ = ·075 Ryd and ·08 Ryd respectively for Be and Mg Following Pickett & Allen

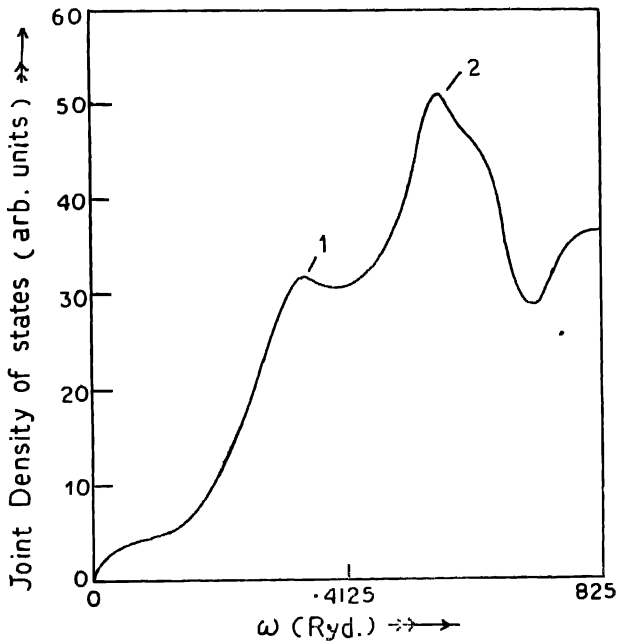


Fig. 2. The JDOS for optical transitions of Be The peaks are · 1 (not sharply defined) and 2 (the only prominent peak).

(1975), we list here the bands chiefly responsible for, and the location in $\boldsymbol{k}$-space where, the important peaks occur, together with the frequencies they correspond to :

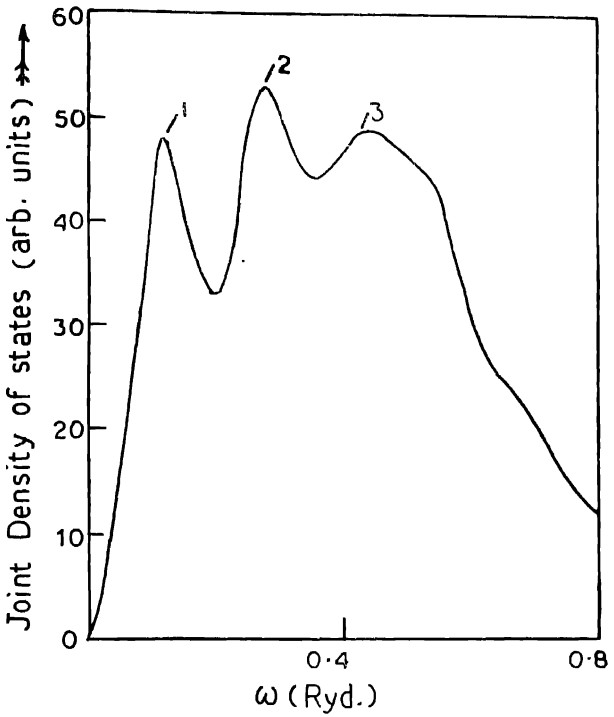


Fig. 3. The JDOS for optical transitions of Mg The peaks are numbered 1, 2, & 3.

*For Beryllium*

*Peak* 1 ($\omega$ between ·3 and ·375 Ryd ). This peak which is not sharply defined, is chiefly caused by transitions (a) from band 1 to 4 along the line joining $k = (\cdot5, 0, \cdot4)$ and $(\cdot3, \cdot3, \cdot4)$, (b) from band 2 to 3 and a part of 4 along the line with $k$ values between $(\cdot5, 0, \cdot3)$ and $(\cdot3, \cdot3, \dot{\cdot}3)$ and (c) from band 2 to 3 along the line joining $k = (\cdot2, 0, \cdot1)$ and $(\cdot13, \cdot13, \cdot1)$.

*Peak* 2. ($\omega$ between ·525 and ·6 Ryd). This is the only prominent peak in the JDOS for Be. It is chiefly caused by transitions (a) along the $T''$-axis, (b) from band 1 to 3 and 4 between $(\cdot5, 0, \cdot2)$ and $(\dot{\cdot}3, \dot{\cdot}3, \cdot2)$, (c) from band 2 to 3 and 4 between $k = (\cdot5, 0, \cdot1)$ and $(\dot{\cdot}3, \dot{\cdot}\bar{3}, \cdot1)$, (d) from band 1 to 3 along $k = (\cdot4, 0, \cdot3)$ and $(\cdot26, \cdot26, \cdot3)$ and (e) from band 1 to 4 along the line joining $(\cdot4, 0, \cdot4)$ and $(\cdot2\dot{6}, \cdot26, \cdot4)$.

*For Magnesium* :

*Peak* 1. ($\omega$ between ·08 and ·16 Ryd.) arises mainly due to transitions (a) between bands 1 and 2 along the $S'$-axis, (b) between bands 1, 2 and 3, 4 along the line joining $= (\cdot 5,\ 0,\ \cdot 4)$ and $(\cdot 3,\ \dot{\cdot 3},\ \cdot 4)$ and (c) between bands 2 and 3 all over the plane passing through and limited by the $k$-points $(\cdot 4,\ 0,\ 0)$, $(\cdot 4,\ 0,\ \cdot 3)$, $(\dot{\cdot 2}6,\ \dot{\cdot 2}6,\ 0)$ and $(\dot{\cdot 2}6,\ \dot{\cdot 2}6,\ \cdot 3)$.

*Peak* 2. ($\omega$ between ·24 and ·32 Ryd.) is mainly due to transitions (a) from band 1 to 4 along the line joining $k = (\cdot 5,\ 0,\ \cdot 3)$ and $(\dot{\cdot 3},\ \cdot 3,\ \cdot 3)$, (b) from band 2 to 3 and 4 along the $k$-values given by $(\cdot 5,\ 0,\ \cdot 2)$ and $(\cdot 3,\ \dot{\cdot 3},\ \cdot 2)$, (c) from band 2 to 3 between $k = (\cdot 3,\ 0,\ \cdot 3)$ and $(\dot{\cdot 1}9,\ \cdot 19,\ \cdot 3)$, (d) from 2 to 4 between $k = (\cdot 4,\ 0,\ \cdot 4)$ and $(\cdot 26,\ \dot{\cdot 2}6,\ \cdot 4)$ and (e) from band 1 to 2 along $(\cdot 4,\ 0,\ \cdot 5)$ and $(\dot{\cdot 2}6,\ \cdot 26,\ \cdot 5)$.

*Peak* 3 ($\omega$ between ·4 and ·48 Ryd.) is caused mainly by transitions (a) along the $T''$-axis, (b) along the line joining $k = (\cdot 5,\ 0,\ \cdot 1)$ and $(\cdot 3,\ \cdot 3,\ 1)$, (c) between bands 1 and 3 all over the plane passing through and limited by $k = (\cdot 4,\ 0,\ 0)$, $(\cdot 4,\ 0,\ \cdot 3)$, $(\cdot 26,\ \cdot 26,\ 0)$ and $(\cdot 26,\ \dot{\cdot 2}6,\ \cdot 3)$ and (d) between 1 and 4 along the $k$-values lying between $(\cdot 4,\ 0,\ \cdot 4)$ and $(\cdot 26,\ \dot{\cdot 2}6,\ \cdot 4)$

In figures (4) and (5), we display a contour plot of the DEDOS of Be and Mg, i.e $I(E, E')$, calculated on a grid of energies of width $\Delta E = \cdot 025$ and ·02 Ryd. for Be and Mg and using 216 microhexagons of the irreducible 1/24th part of the BZ. The DOS curves of Be and Mg are plotted along both the axes of figures (4) and (5) respectively. The energies (in Rydbergs) are measured relative to the muffin-tin zero. The Fermi energies ($-1{\cdot}008$ Ryd and $-0{\cdot}958$ Ryd. respectively for Be and Mg (Chatterjee & Sinha 1975) are shown by dotted lines in the figures. The region not shown in the contour diagrams correspond to $E$ and $E'$ near the top of the conduction bands or the bottom of the valence bands and hence contain very few transitions The peaks and the initial and final energies at which they occur are readily identifiable from the figures. The $\omega$ values at which such peaks occur are found to correspond satisfactorily to the $\omega$ values given from the corresponding JDOS curves of figures 2 and 3

## 4 Discussion

We have used the APW calculations of the energy bands of Be and Mg to study their optical properties. It would have been interesting to compare our results with the optical properties obtained from OPW band calculations Unfortunately, the OPW calculations for Be and Mg by Loucks & Cutler (1964) and Falicov (1962) respectively, do not include a study of the JDOS curves of these metals.

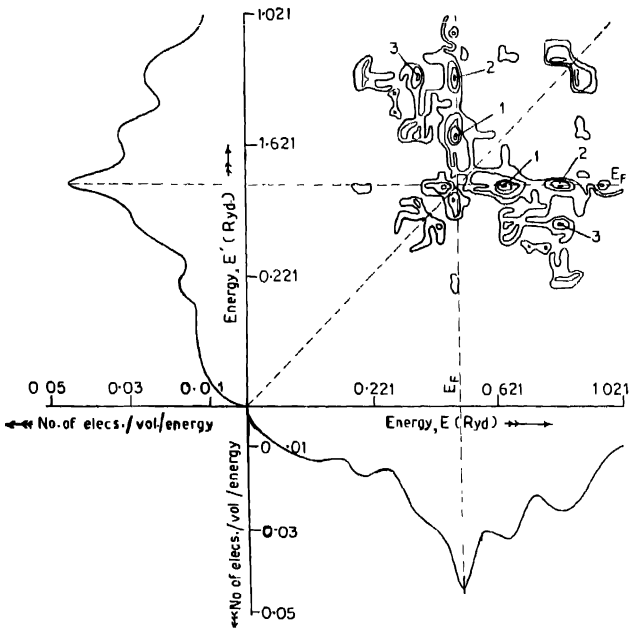


Fig 4 The DEDOS, $I(E = E')$ Be, for the optical transitions between its bands The DOS is plotted along each axis The important peak is numbered '2' and the less important peak '1'. The figure is symmetrical about $E = E'$

Now as has been seen, our calculation allows the association of particular transitions in the BZ with the positions at which structure occurs in the JDOS curve. We observe that Be, whose energy bands deviate markedly from those of free electrons, shows only one peak in its JDOS curve, while Mg, which is free electron-like has three well-defined peacks. The results further indicate that such peaks can arise from transitions away from the symmetry points and axes in the BZ.

Finally, it may be pointed out that the JDOS curves presented in this paper not only help to predict the optical properties of Be and Mg, but also suggest the nature of variation of the imaginary part of their dielectric constants for inter-band transitions with the frequency of the exciting radiation. In view of the recent experiments of Weaver *et al* (1973, 1974) on the dielectric functions of bcc metals, this may be of considerable importance to workers engaged in similar experiments with metals of hcp structure.

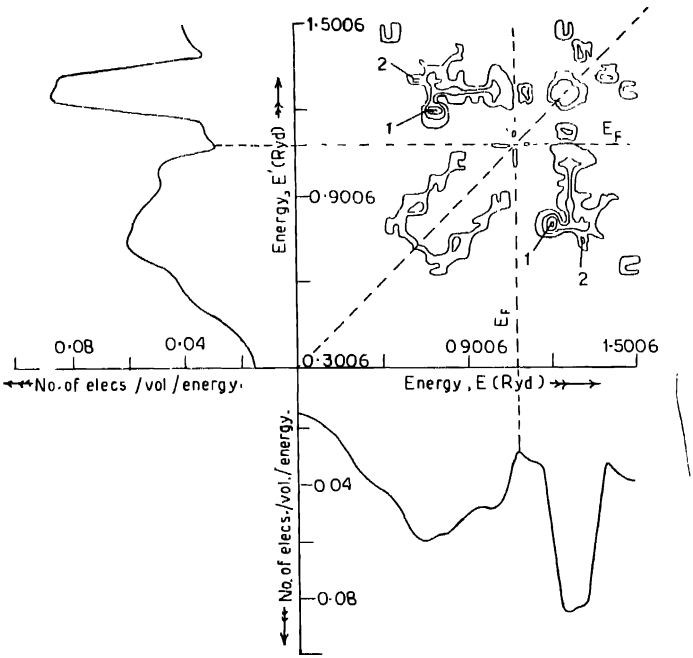


Fig. 5 The DEDOS, $J(E, E')$ for Mg, for the optical transitions between it bands The DOS is plotted along each axis The important peaks are numbered 1, 2 & 3 The figure is symmetrical about $E = E'$.

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## References

Chatterjee S. & Sinha Parsathi 1975 *J. Phys F : Metal Phys* **I**, 638
Dommock J O. 1971 *Solid State Physics* **26**, 103
Falicov L. M 1962 *Phil, Trans, R Soc.* **A255**, 55.
Gilat G & Raubenheimer L J. 1966 *Phys Rev* **144**, 390
Harrison W A 1962 *Phys. Rev* **126**, 497
Janak J F. 1971 *Coompudational Methods in Band Theory*, edited by Marcus P M , Janak J F. and Williams A R. Plenum Press, New York, London.
Koelling D D., Mueller F M , & Veal B W 1974 *Phys. Rev* **B10**. 1290.
Loucks T L & Cutler P. H 1964 *Phys Rev* **133**, A819.
Pickett W. E. & Allen P B 1975 *Phys. Rev.* **B11**, 3599
Sinha Parsathi & Chatterjee S. 1977 *J. Phys F : Metal Phys* **7** 105
Stark R. W. & Falicov L. M. 1967 *Phys Rev. Letters* **19**, 795.
Terrell J. M 1964 *Phys. Lett.* **8**, 149
———— 1966 *Phys. Rev.* **149**, 256
Weaver J H., Lynch D W. & Olson C. G. 1973 *Phys Rev* **B7**, 4311
———— 1974 *Phys Rev.* **B10**, 501.